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## (54) Novel boron-containing compositions and lubricants containing them

(67) Boron-containing compositions are prepared by the reaction of boric acid, boron trioxide, a boron halide or an ester of boric acid with the

condensation product at the formula A (which may be formed in situ) of a hydroxyaromatic compound (preferably an alkylphenol) with an aliphatic aldehyde (preferably formaldehyde). The resulting composition is thought to contain compound of the formula II

They are useful as lubricant additives to inhibit oxidation, improve extreme pressure properties and decrease fuel consumption. They are especially

useful as oxidation inhibitors in gear and bearing lubricants containing substantial amounts of sulfur and phosphorus compounds.

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## Novel boron-containing compositions and lubricants c ntaining them

This invention relates to compositions useful as additives for lubricants, especially industrial gear oils; to a method for the preparation of such compositions; and to additive concentrates and lubricants containing them. In their most general sense, the compositions of this invention are b ron-containing compositions prepared by reacting, at a temperature within the range of about 70—250°C.:

(A) at least one compound of the formula

wherein R¹ is hydrogen or a lower alkyl-based radical, R² is hydrogen or an aliphatic hydrocarbon-based radical free from acetylenic unsaturation and Ar is an aromatic hydrocarbon-based radical; and

(B) at least one of boric acid, boron trioxide, boron halides and esters of boric acid.

Recent developments in the area of machinery operation have materially increased the demands made on lubricants for use in such machinery. For example, increases in the price of gasoline and other fuels and sporadic shortages of such fuels have increased the necessity for lubricant additives which promote fuel economy. In the area of gear lubricants, it has been necessary to develop additives which improve operation under conditions of extreme pressure.

A further area of increasing demand on gear and bearing lubricants, particularly for industrial use, relates to formation of deposits through oxidation. Such deposits frequently form, especially in lubricants containing substantial amounts of phosphorus and sulfur compounds of the type commonly used as gear lubricant additives. The deposits increase the susceptibility of the machinery to damage and decrease the efficiency of the lubricant. It is therefore of interest to develop improved oxidation inhibitors which decrease deposit formation in lubricants, especially gear lubricants for industrial use.

As will be apparent from the brief description hereinabove, the boron-containing compositions of this invention are prepared from two reagents. Reagent A is at least one compound having Formula I.

Such compounds may conveniently be prepared by the reaction of (A—1) at least one aliphatic aldehyde-releasing compound corresponding to an aldehyde having the formula R¹CHO with (A—2) at least one hydroxyaromatic compound having the formula R²—ArOH.

As used in the description of these compounds, the term "hydrocarbon-based radical" denotes a radical having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character within the context of this invention. Such radicals include the following:

(1) Hydrocarbon radicals; that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl or cycloalkenyl), aromatic, aliphatic- and alicyclic-substituted aromatic, aromatic-substituted aliphatic and alicyclic radicals, and the like. Such radicals are known to those skilled in the art; examples are methyl, ethyl, propyl, hexyl, decyl, octadecyl, phenyl, tolyl, naphthyl, hexenyl, dodecenyl and octadecenyl (all isomers being included).

(2) Substituted hydrocarbon radicals; that is, radicals containing non-hydrocarbon substituents which, in the context of this invention, do not alter the predominantly hydrocarbon character of the radical. Those skilled in the art will be aware of suitable substituents; examples are halo (especially chloro and bromo), hydroxy, alkoxy, alkylthio, nitro and carbalkoxy.

(3) Hetero radicals; that is, radicals which, while predominantly hydrocarbon in character within the context of this invention, contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms will be apparent to those skilled in the art and include, for example, nitrogen, oxygen and sulfur.

In general, no more than about three substituents or hetero atoms, and preferably no more than one, will be present for each 10 carbon atoms in the hydrocabron-based radical.

Terms such as "alkyl-based radical" and the like have meanings analogous to the above with respect to alkyl radicals and the like.

Preferably, the hydrocarbon-based radicals in the compounds of this invention are free from acetylenic and usually also from ethylenic unsaturation. The radicals are usually hydrocarbon and certain of them may be lower hydrocarbon, the work "lower" denoting radicals containing up to seven carbon atoms.

Reagent A—1, the aliphatic aldehyde-releasing compound, may be either a free aldehyde (e.g., formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde), an acetal thereof (e.g., formal, acetaldehyde diethyl acetal), or a reversible polymer thereof (e.g., trioxane, paraformaldehyde, paraldehyde). Preferred as reagent A—1 are aldehyde-releasing compounds corresponding to aldehydes in which R² is hydrogen or methyl and especially hydrogen. Thus, the preferred aldehydes are formaldehyde and acetaldehyde, especially the former.

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Reagent A—2 is at least one hydroxyaromatic compound having the formula R<sup>2</sup>—ArOH, in which R<sup>2</sup> may be hydrogen or an aliphatic hydrocarbon-based radical free from acetylenic unsaturation. Most often, R<sup>2</sup> is a hydrocarbon-based radical containing about 4—200 and especially about 6—100 carbon atoms. It is preferably an alkyl radical containing about 10—100 and most desirably about 10—40 carbon atoms. From the standpoint of availability and particular suitability to the purposes of this invention, compounds in which R<sup>2</sup> is an alkyl radical containing about 15—30 carbon atoms are particularly contemplated.

The Ar radical is an aromatic hydrocarbon-based radical, typically derived from such aromatic compounds as benzene, naphthalene, biphenyl, diphenylmethane and diphenyl sulfide. Thus, the hydroxyaromatic compound may be, for example, phenol, a naphthol, an alkylphenol or alkylnaphthol, or a sulfur- and/or methylene-bridged phenol or alkylphenol. Suitable sulfur-bridged phenols may be prepared by the reaction of sulfur dichloride with the corresponding phenol or alkylphenol. Methylene-bridged phenols may be prepared by a similar reaction with a formaldehyde-releasing reagent, which may be at the same time as the reaction with reagent A—1 (which is, of course, preferably also a formaldehyde-releasing reagent) or before or after that reaction.

The alkylphenois are preferred for use as reagent A—2, and especially those containing at least one unsubstituted ortho or para carbon atom, preferably ortho. Especially preferred are compounds in which Ar is a phenylene radical (i.e., —C<sub>6</sub>H<sub>4</sub>—) and most desirably o-phenylene. Such compounds are typically prepared by the known alkylation of phenois with various olefins, alkyl halides and the like, including commercial mixtures of such olefins and alkyl halides.

By convention, the "Ar" radical includes within its structure all hydrogen atoms bonded directly to an aromatic ring. Thus, all aromatic carbon atoms not bonded to some other part of the molecule or to a substituent, specified or unspecified, are understood to be bonded to hydrogen atoms.

The reaction of reagents A—1 and A—2 is a known reaction; it is frequently effected in the presence of an acidic or basic catalyst. Reactions of this type are disclosed, for example, in U.S. Patent 4,147,643, which is incorporated by reference herein for such disclosure.

Reagent B in the method of this invention is at least one of boric acid, boron trioxide (B<sub>2</sub>O<sub>3</sub>), boron halides (especially boron trichloride, BCI<sub>3</sub>) and esters of boric acid. Boron trioxide will react first with water formed in the reaction of reagents A—1 and A—2 to form boric acid, which then reacts further.

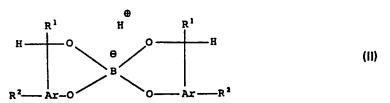
30 Any of the various forms of boric acid may be used, including metaboric acid (HBO<sub>2</sub>), orthoboric acid (H<sub>3</sub>BO<sub>3</sub>) and tetraboric acid (H<sub>2</sub>B<sub>4</sub>O<sub>7</sub>). The esters of these acids include, for example, the methyl, ethyl and propyl esters, with the methyl esters being most readily available and therefore most often used. Boric acid, and especially orthoboric acid, is preferred for use as reagent B.

The method of this invention involves reacting reagents A and B at a temperature within the range of about 70—250°C., preferably about 90—150° and most often about 90—130°C. It is often preferred to form reagent A in situ by heating a mixture of reagents A—1, A—2 and B. The reaction is frequently effected in the presence of a substantially inert, normally liquid organic diluent, typically an aromatic hydrocarbon such as toluene or xylene, a chlorinated aromatic hydrocarbon such as chlorobenzene or an ether such as ethylene glycol dimethyl ether.

When formaldehyde or a formaldehyde-releasing compound is used as reagent A—1, a portion thereof is sometimes lost by volatilization during the reaction. It is therefore preferred to use reagent A—1 in excess. Most often, about 1.5—8.0 moles of reagent A—1 and about 1.0—2.5 moles of reagent A—2 are used per mole of reagent B.

The reaction is frequently effected in the presence of (C) an acidic catalyst. Suitable acidic catalysts include acid-form anion exchange resins, sulfonic acids such as benzenesulfonic and ptoluenesulfonic acids, and alkanoic acids such as acetic, propionic, butyric and valeric acids. The lower alkanoic acids and especially propionic acid are preferred. The amount of reagent C is typically less than 0.5 mole, most often about 0.1—0.3 mole, per mole or reagent A—1.

The molecular structures of the boron-containing compositions prepared by the method of this invention are not known with certainty. Most likely, they are mixtures of compounds having a number of molecular structures. However, there is strong evidence of the presence therein of compounds having the formula



wherein R<sup>1</sup>, R<sup>2</sup> and Ar are as previously defined. Therefore, the present invention also includes boron-containing compositions comprising at least one compound having formula II.

The preparation of the boron-containing compositions of this invention is illustrated by the following examples. All parts are by weight unless otherwise indicated.

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Example 1

A mixture of 485.7 grams (1 mole) of an alkyl phenol prepared by alkylation of phenol with a commercial mixture of C<sub>24-28</sub> α-olefins, 10 grams (1 mole) of paraformaldehyde, 30.9 grams (0.5 mole) of boric acid, 22.2 grams (0.3 mole) of propionic acid and 600 ml. of toluene is heated under reflux for 3 hours, as water is removed by distillation. An additional 10 grams of paraformaldehyde is added and refluxing is continued for 2 hours; a third 10-gram portion of paraformaldehyde (total 3 moles) is then added and refluxing is continued as water and excess paraformaldehyde are removed. A total of 45 ml. of water is obtained. The mixture is filtered and vacuum stripped to yield the desired product, which contains 1.19% boron.

10 Example 2

A product similar to that of Example 1 is obtained from 1,094 grams (2 moles) of the alkylphenol of Example 1, 120 grams (4 moles) of paraformaldehyde added in two 60-gram increments, 123.6 grams (2 moles) of boric acid, 44.4 grams (0.6 mole) of propionic acid and 700 ml. of toluene. It contains 1.32% boron.

15 Example 3

A mixture of 1,094 parts (2 moles) of the alkylphenol of Example 1, 60 parts (2 moles) of paraformaldehyde, 61.8 parts (1 mole) of boric acid, 44.4 parts (0.6 mole) of propionic acid and 200 parts of toluene is heated under reflux for about 6 hours as water (about 70 parts) is removed by distillation. The mixture is then vacuum stripped and filtered at 110—120°C. to yield the desired 20 product; it contains 0.73% boron.

Example 4

A mixture of 536 parts (1 mole) of the alkylphenol of Example 1, 30 parts (1 mole) of paraformaldehyde, 30.9 parts (0.5 mole) of boric acid and 100 parts of toluene is heated under reflux for 3 hours as water is removed by distillation. A second 30-part increment of paraformaldehyde (total 2 moles) is added and heating under reflux is continued for 5 hours. A total of 48 ml. of water is removed. The mixture is then vacuum stripped and filtered while hot to yield the desired product; it contains 0.89% boron.

Example 5

Following the procedure of Example 1, a product containing 1.75% boron is obtained by the reaction of 792 grams (3 moles) of tetrapropenylphenol, 270 grams (9 moles, added in three 3-mole increments) of paraformaldehyde, 92.7 parts (1.5 moles) of boric acid, 66.6 parts (0.9 mole) of propionic acid and 1,000 ml. of toluene.

Example 6

A mixture of 430 parts (1 mole) of an alkylphenol prepared by alkylation of phenol with a commercial mixture of C<sub>18-24</sub> α-olefins, 30 parts (1 mole) of paraformaldehyde, 30.9 parts (0.5 mole) of boric acid, 22.2 parts (0.3 mole) of propionic acid and 100 parts of toluene is heated under reflux as water is removed by distillation. After 33 ml. of water have been removed, an additional 30 parts of paraformaldehyde is added (total 2 moles) and refluxing is continued as water (total 41 ml.) and paraformaldehyde are removed by distillation. The mixture is vacuum stripped and filtered to yield the desired product; it contains 1.14% boron.

Example 7

A mixture of 1,945 parts (5 moles) of an alkylphenol prepared by alkylation of phenol with a decene dimer, 150 parts (5 moles) of paraformaldehyde, 154 parts (2.5 moles) of boric acid, 88.8 parts (1.2 moles) of propionic acid and 300 parts of toluene is heated under reflux as water is removed by distillation. When 157 parts of water has been removed, an additional 150 parts of paraformaldehyde is added (total 10 moles) and heating is continued until water evolution is complete. The mixture is vacuum stripped and filtered while hot. The filtrate is the desired product; it contains 1.44% boron.

Example 8

A boron-containing composition is prepared by a method similar to that of Example 1 except that 50 trimethyl borate is substituted, on an equimolar basis, for the boric acid.

Example 9

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A boron-containing composition is prepared by a meth d similar to that f Example 1 except that paraldehyde and acetic acid are respectively substituted, on an equimolar basis, for the paraformaldehyde and propionic acid.

As previously indicated, the boron-containing compositions of this invention are useful as additives for lubricants. They are particularly useful as oxidation inhibitors and extreme pressure agents in gear and bearing lubricants; however, they may also be used in internal combustion engine lubricants to reduce fuel consumption. They can be employed in a variety of lubricants based on diverse

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oils of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof. In addition to gear and bearing lubricants, the boron-containing compositions may be used in crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, including automobile and truck engines, two-cycle engines, aviation piston engines, marine and railroad diesel engines, and the like. The boron-containing compositions can also be used in gas engines, stationary power engines and turbines and the like. Automatic transmission fluids, transaxle lubricants, metalworking lubricants, hydraulic fluids and other lubricating oil and grease compositions can also benefit from the incorporation therein of the boron-containing compositions.

Natural oils include liquid petroleum oils and solvent-treated, acid-treated and/or hydrorefined mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins [e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)]; alkylbenzenes [e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes]; polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); and alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of 500—1000, diethyl ether of polypropylene glycol having a molecular weight of 1000—1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C<sub>3</sub>—C<sub>8</sub> fatty acid esters and C<sub>13</sub> Oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of these esters include dibutyl adipate, dl(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, dlisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters useful as synthetic oils also include those made from  $C_5$  to  $C_{12}$  monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxysiloxane oils and silicate oils comprise another useful class of synthetic lubricants; they include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-tert-butylphenyl) silicate, hexa-(4-methyl-2-pentoxy) disiloxane, poly(methyl) siloxanes and poly(methylphenyl) siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

Unrefined, refined and rerefined oils can be used in the lubricants of the present invention.

Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly form distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

Generally, the lubricants of the present invention contain an amount of the boron-containing composition sufficient to inhibit oxidation, improve extreme pressure properties or decrease fuel consumption. Normally this amount will be about 0.1—5.0%, pr ferably about 0.5—2.5% and most often about 0.5—1.5% by weight.

The invention also contemplates the use of other additives in combination with the boron-containing compositions. Suitable additives for internal combustion engine lubricants include, for example, detergents and dispersants of the ash-producing or ashless type, corrosion-inhibiting and auxiliary oxidation-inhibiting agents, pour point depressing agents, extreme pressure agents, color stabilizers and anti-foam agents.

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The ash-producing detergents are exemplified by oil-soluble neutral and basic salts of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, and organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage including those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a molecular weight of 1000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium, strontium and barium.

The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The commonly employed methods for preparing the basic salts involve heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or suifide at a temperature above 50°C. and filtering the resulting mass. The use of a "promoter" in the neutralization step to aid the incorporation of a large excess of metal likewise is known. Examples of compounds useful as the promoter include phenolic substances such as phenol, napthol, alkylphenols, thiophenol, suifurized alkylphenols, and condensation products of formaldehyde with phenolic substances; alcohols such as methanol, 2-propanol, octyl alcohol, Cellosolve, Carbitol, ethylene glycol, stearyl alcohol and cyclohexyl alcohol; and amines such as aniline, phenylenediamine, phenothiazine, phenyl-β-naphthylamine and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralizing agent and at least one alcohol promoter, and carbonating the mixture at an elevated temperature such as 60—200°C.

Ashless detergents and dispersants are so called despite the fact that, depending on its constitution, the dispersant may upon combustion yield a non-volatile material such as boric oxide or phosphorus pentoxide; however, it does not ordinarily contain metal and therefore does not yield a metal-containing ash on combustion. Many types are known in the art, and any of them are suitable for use in the lubricants of this invention. The following are illustrative:

(1) Reaction products of carboxylic acids (or derivatives thereof) containing at least about 34 and preferably at least about 54 carbon atoms with nitrogen-containing compounds such as amine, organic hydroxy compounds such as phenois and alcohols, and/or basic inorganic materials. Examples of these "carboxylic dispersants" are described in many U.S. patents including 3,272,746; 3,381,022; and 4,234,435.

(2) Reaction products of relatively high molecular weight aliphatic or alloyclic halides with amines, preferably polyalkylene polyamines. These may be characterized as "amine dispersants" and examples thereof are described for example, in U.S. patents 3,275,554; 3,438,757; 3,454,555; and 3,565,804.

(3) Reaction products of alkyl phenols in which the alkyl group contains at least about 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines), which may be characterized as "Mannich dispersants". The materials described in U.S. patents 3,368,972; 3,413,347; and 3,980,569 and illustrative.

(4) Products obtained by post-treating the carboxylic, amine or Mannich dispersants with such reagents as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, phosphorus compounds or the like. Exemplary materials of this kind are described in a number of U.S. patents.

(5) Interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., aminoalkyl acrylates or acrylamides and poly-(oxyethylene-substituted acrylates. These may be characterized as "polymeric dispersants" and examples thereof are disclosed in U.S. patents 3,329,658; 3,449,250; 3,519,565; 3,666,730; 3,687,849; and 3,702,300.

All of the above-noted patents are incorporated by reference herein for their disclosures of ashless dispersants.

Extreme pressure agents and corrosion-inhibiting and auxiliary oxidation-inhibiting agents are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated wax; organic sulfides and polysulfides such as benzyl disulfide, bis(chlorobenzyl) disulfide, dibutyl tetrasulfide, sulfurized methyl oleate, sulfurized alkylphenols, sulfurized dipentene, and sulfurized terpenes; phosphosulfurized hydrocarbons such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate; phosphorus esters including principally dihydrocarbon and trihydrocarbon phosphites such as dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite, dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite, dimethyl naphthyl phosphite, oleyl 4-pentylphenyl phosphite, polypropylene (molecular weight 500)-substituted phenyl phosphite and diisobutyl-substituted phenyl phosphite; metal thiocarbamates such as zinc dioctyldithiocarbamate and barium heptylphenyl dithiocarbamate; Group II metal phosphorodithioates such as zinc dicyclohexyl-phosphorodithioate, zinc dioctylphosphorodithioate, barium di(heptylphenyl)phosphorodiethioate, cadmium dinonylphosphorodithioate, and the zinc salt of a phosphorodiethioic acid produced by the reaction of phosphorus pentasulfide with an equimolar mixture of isopropyl alcohol and n-hexyl alcohol.

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Gear and bearing lubricants according to this invention may contain the boron-containing composition in combination with known gear lubricant additive packages. These packages frequently contain substantial amounts, effective to improve the extreme pressure properties thereof of sulfur and phosphorus compounds. Many sultable gear lubricant additive packages of this type are known to those skilled in the art. The boron-containing compositions are particularly effective as a xidation inhibitors in such lubricants containing relatively high sulfur and phosphorus levels.

The boron-containing compositions of this invention may be, and frequently are, added directly to the otherwise fully formulated lubricant prior to use. However, they may also be diluted with a substantially inert, normally liquid organic diluent such as mineral oil, naphtha, benzene, toluene or xylene to form an additive concentrate. These concentrates may contain from about 10% to about 90% by the weight of the boron-containing composition and may contain, in addition, one or more other additives known in the art or described hereinabove.

The following is illustrative of a gear and bearing lubricant of this invention. All parts are by weight.

15	Mineral oil	97.89 parts	15
	Product of Example 1	0.75 part	
	Soybean oil	0.25 part	
	Sulfurized isobutene	0.62 part	
	Amine-neutralized phosphate	·	4
20	ester of hydroxyalkyl		20
	dialkylphosphorodithioate	0.40 part	7
	Polyoxyalkylene demulsifier	0.005 part	•
	N-Tridecyltrimethylenediamine	0.05 part	
	Tolyltriazole	0.015 part	
25	Silicone anti-foam agent	0.02 part	25

## Claims

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1. A method for preparing a boron-containing composition which comprises reacting, at a temperature within the range of about 70—250°C.:

(A) at least one compound of the formula

wherein R<sup>1</sup> is hydrogen or a lower alkyl-based radical, R<sup>2</sup> is hydrogen or an aliphatic hydrocarbon-based radical free from acetylenic unsaturation and Ar is an aromatic hydrocarbon-based radical and

- (B) at least one of boric acid, boron trioxide, boron halides and esters of boric acid.

  2. A method according to claim 1 wherein reagent A is formed in situ by the reaction of (A—1) at least one aliphatic aldehyde-releasing compound corresponding to an aldehyde having the formula R¹CHO with (A—2) at least one hydroxyaromatic compound having the formula R²—Ar—OH.
- 3. A method according to claim 2 wherein Ar contains at least one unsubstituted ortho or para carbon atom.
- 4. A method according to claim 3 wherein Ar contains at least one unsubstituted ortho carbon 40 atom.
  - 5. A method according to claim 3 wherein Ar is a phenylene radical.
  - 6. A method according to claim 5 wherein Ar is an o-phenylene radical.
  - 7. A method according to claim 6 wherein R<sup>1</sup> is hydrogen or methyl.
- 8. A method according to claim 7 wherein R<sup>2</sup> is a hydrocarbon-based radical containing about
  45. 4—200 carbon atoms.
  - 9. A method according to claim 8 wherein R<sup>2</sup> is an alkyl radical containing about 10---100 carbon atoms.
  - 10. A method according to claim 9 wherein R<sup>2</sup> is an alkyl radical containing about 10—100 carbon atoms.
    - 11. A method according to claim 10 wherein R<sup>2</sup> contains about 10—40 carbon atoms.

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      12. A method according to claim 11 wherein R<sup>1</sup> is hydrogen.
  - 13. A method according to claim 12 wherein reagent B is orthoboric acid and the reaction temperature is in the range of about 90—150°C.
    - 14. A method according to claim 13 wherein R<sup>2</sup> contains about 15—30 carbon atoms.
- 55 15. A method according to claim 1, 2, 4, 6, 8, 11, 13 or 14 wherein the reaction is effected in the presence of (C) an acidic catalyst.

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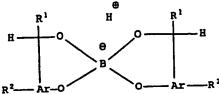
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16. A method according to claim 15 wherein reagent C is an alkanoic acid.
17. A method according to claim 16 wherein reagent C is a lower alkanoic acid.
18. A method according to claim 17 wherein reagent C is propionic acid.
19. A method according to claim 2, 4, 6, 8, 11, 13 or 14 wherein about 1.5—8.0 moles of
5 reagent A—1 and about 1.0—2.5 moles of reagent A—2 are used per mole of reagent B.
20. A method according to claim 15 wherein about 1.5—8.0 moles of reagent A—1 and about 1.0—2.5 moles of reagent A—2 are used per mole of reagent B.
21. A method according to claim 17 wherein about 1.5—8.0 moles of reagent A—1 and about 1.0—2.5 moles of reagent A—2 are used per mole of reagent B.
22. A composition prepared by the method of claim 1, 2, 4, 6, 8, 11, 13 or 14.
23. A boron-containing composition comprising at least one compound having the formula



wherein R<sup>1</sup> is hydrogen or a lower alkyl-based radical, R<sup>2</sup> is hydrogen or an aliphatic hydrocarbon-based radical free from acetylenic unsaturation, and Ar<sup>2</sup> is an aromatic hydrocarbon-based radical.

24. A composition according to claim 23 wherein Ar is bonded to the rest of the molecule through ortho or para positions.

25. A composition according to claim 23 wherein Ar is bonded to the rest of the molecule through ortho positions.

26. A composition according to claim 24 wherein Ar is a phenylene radical.

27. A composition according to claim 26 wherein Ar is an o-phenylene radical.

28. A composition according to claim 27 wherein R<sup>1</sup> is a hydrogen or methyl.

29. A composition according to claim 28 wherein R<sup>2</sup> is a hydrocarbon-based radical containing about 4—200 carbon atoms.

30. A composition according to claim 29 wherein R<sup>2</sup> contains about 6---100 carbon atoms.

25 31. A composition according to claim 30 wherein R<sup>2</sup> is an alkyl radical containing about 10—100 25 carbon atoms.

32. A composition according to claim 31 wherein R<sup>2</sup> contains about 10---40 carbon atoms.

33. A composition according to claim 32 wherein R¹ is hydrogen.

34. A composition according to claim 33 wherein R<sup>2</sup> contains about 15—30 carbon atoms.

35. An additive concentrate comprising a substantially inert, normally liquid organic diluent and about 20—90% by weight of a composition according to claim 22.

36. An additive concentrate comprising a substantially inert, normally liquid organic diluent and about 20—90% by weight of a composition according to any of claims 23—34.

37. A lubricating composition comprising a major amount of a lubricating oil and about 0.1—35 5.0% by weight of a composition according to claim 22.

38. A composition according to claim 37 which also contains minor amounts, effective to improve the extreme pressure properties thereof, of sulfur and phosphorus compounds.

39. A lubricating composition comprising a major amount of a lubricating oil and about 0.1—5.0% by weight of a composition according to any of claims 23—34.

40. A composition according to claim 39 which also contains minor amounts, effective to improve the extreme pressure properties thereof, of sulfur and phosphorus compounds.

41. The invention in its several novel aspects.